ALKALI-ACTIVATED FLY ASH COMPOSITES WITH CANINE-FIBRE REINFORCEMENT

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The construction industry contributes over 40% of human-made carbon emissions, due mainly to the high consumption of raw materials and energy-intensive processing. Alkali-activated materials (AAMs) prepared from secondary raw materials such as fly ash (FA) offer a sustainable alternative that is synthesised at low temperatures. In this study, the FA was milled and sieved to achieve higher reactivity and compressive strength (CS). To increase the bending strength, keratin-based fibres from a Chesapeake Bay Retriever were added in mass percentages (m%) of 1 and 5. While the addition of 1 m% of fibres improved the overall mechanical performance and increased the CS by ~20 MPa, the addition of 5 m% resulted in a soft composite that deforms under pressure but returns to its original shape cyclically as the fibres act as an internal cushioning network. However, the CS of the 5 m% fibre-rich composite decreased to 20 MPa, which is 30 MPa lower than the fibre-free sample.

Keywords:
alkali-activated materials,
fly ash,
keratin-based fibres,
Chesapeake Bay Retriever,
circular economy

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1 Introduction

The construction and civil engineering industry has a significant impact on the environment, contributing over 40% of human-made carbon emissions (*The Industry Creating a Third of the World's Waste*, n.d.), due mainly to the high consumption of raw materials and energy-intensive processing at temperatures above 1000 °C (*Cement Production: How Hot Air Becomes Green Energy*, n.d.).

Alternative materials such as alkali-activated materials (AAMs) are being researched, to reduce the impact on the environment. AAMs can be synthesised from secondary raw materials, often at low temperatures. They represent a more sustainable alternative to conventional cement, and could transform the built environment from a net carbon emitter to a carbon sink (Škvára, 2007).

Alkali activation requires precursors rich in amorphous silicon and aluminium, which form a three-dimensional aluminosilicate network connected by oxygen bridges. The charge imbalance around the aluminium is compensated by the alkali elements (chemical elements from the 1st and 2nd groups of the periodic table) from the liquid alkali reagent (Škvára, 2007). Materials rich in Si and Al include fly ash (FA), a by-product of coal combustion (Horvat et al., 2023; Palomo & Fernández-Jiménez, 2011). However, despite the chemical suitability of FA for alkali activation, FA has physical limitations. The predominantly spherical morphology of FA particles lacks fibrous structures (Horvat et al., 2022), which would contribute naturally to higher bending strength (Traven et al., 2022).

Fibres can be added to overcome the natural physical limitation of the FA. In conventional building materials, synthetic fibres such as polypropylene (Blazy & Blazy, 2021) or steel (Batson, 1976) are used commonly. However, synthetic fibres are not sustainable, as they are made from raw materials, are not recyclable, increase the environmental footprint and the cost of the composite.

Hence, natural fibres are a promising alternative. In the past, animal hairs have been used as reinforcement in mortars and plasters (Dudac, 2019) as they provide mechanical support and durability. However, the behaviour of keratin-based fibres permanently embedded in an alkaline matrix has not been studied systematically, and their performance in AAMs is still largely unknown.

Therefore, this study focuses on the evaluation of the mechanical performance of alkali-activated FA composites reinforced with keratin-based fibres from a Chesapeake Bay Retriever. The presented results demonstrate the potential for environmentally sustainable, high-performance construction materials that utilise unused waste resources.

2 Experimental

2.1 Materials and characterisation of the materials

In the alkali-activated synthesis of the composite, two solid (Figure 1) and one liquid ingredients were used: FA as the precursor, keratin-based hair as the fibres, and an Na-silicate solution as the liquid alkali:

- The precursor used for alkali activation was FA from the Slovenian thermal power plant. The FA was milled and sieved below 125 μm to increase the reactivity in alkaline media. However, as-received FA (labelled as FA) was used as the primary AAM reference for the milled FA (labelled as FA_{milled}) and for the AAMs containing fibres.
- The keratin-based fibres were hairs trimmed from brown short-coated Chesapeake Bay Retrievers (bred under the rules of the Kennel Club of Slovenia and according to the Fédération Cynologique Internationale breed standard) during the shedding period after winter. The collected hair was cut to a length of up to 1 cm.
- The liquid alkali was an Na-silicate solution (Geosil, 344/7, Woelner, 16.9 m% Na_2O, 27.5 m% SiO_2, 55.6 m% H_2O), which was used without further manipulation.

The FA was characterised using complementary analytical techniques, to assess both the chemical and mineralogical composition as well as the organic content: loss on ignition (LOI), X-ray fluorescence (XRF), and X-ray diffraction (XRD):

- The organic residues were quantified by LOI at 550 °C for 2 h.
- The bulk chemical composition, covering elements from fluorine to americium, was determined by XRF (Thermo Scientific ARL Perform'X Sequential XRF)

on samples milled and sieved below 125 μm and treated thermally at 950 °C for 2 h.

- The mineral phases were identified by XRD (Empyrean PANalytical Diffractometer, Cu source) over a 2θ range of 4–70° with a step size of 0.0263°, using Rietveld refinement with X'Pert Highscore plus 4.1 software and corundum (Al_2O_3) as an external standard. The crystalline and amorphous fractions were estimated by comparing the XRD and XRF results element-wise. A detailed summary of the FA characterisation results is provided in Table 1, and all the raw data are available in the open repository.

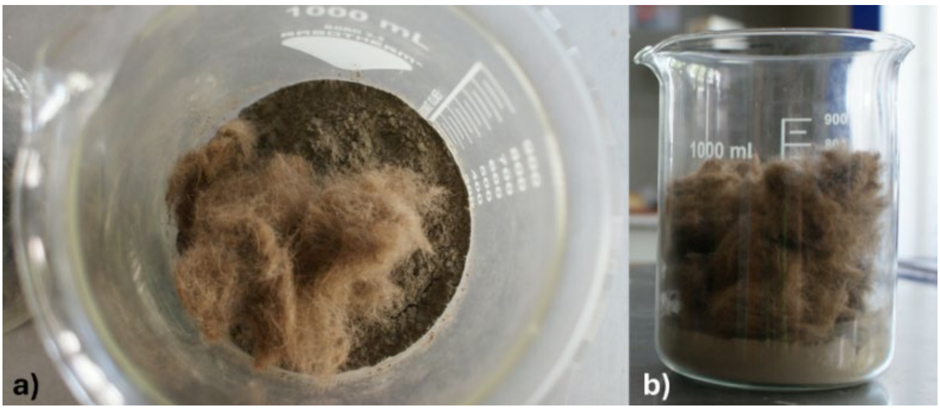

Figure 1: Solid dry ingredients: FA_{milled} at the bottom of the beaker, with a) 1 m%, and b) 5 m% of CBR fibres on top.

Source: own.

Table 1: Content of critical elements for alkali activation in the FA, expressed in mass percent (m%).

Elements [m%]	Na	K	Mg	Ca	Al	Si	Content [m%]
XRF (whole material)	0.7	2.0	1.5	6.3	14.1	20.4	100.0
XRD (crystalline)	0.0	0.0	0.6	0.9	3.2	4.4	25.1
Amorphous	0.7	2.0	0.9	5.4	10.9	16.0	74.9

The mechanical properties (compressive strength, bending strength and geometric density) were evaluated on 3-day-old AAMs using a ToniTechnik ToniNORM testing machine.

2.2 Synthesis of the material

The mixture of FA (and FA_{milled}) and the alkali solution was designed based on the XRF and XRD measurements of the FA, excluding its organic content. The calculation was performed under boundary conditions aimed at avoiding efflorescence with subsequent degradation of the AAM (the ratio of Al to the combined content of chemical elements from the first group of the periodic table was kept close to 1 or slightly lower) and achieving the highest compressive strength (the molar ratio of the amorphous Si to Al was set to 1.9 to 1). The theoretical mass ratio between the FA and liquid alkali was established at 1 to 0.35. The optimal ratio was determined using software developed on the MS Excel platform within the Project no. C3330-17-529032 "Raziskovalci-2.0-ZAG-529032" (Horvat & Ducman, 2019), and later upgraded in the ARIS project under Grant no. J2-3035.

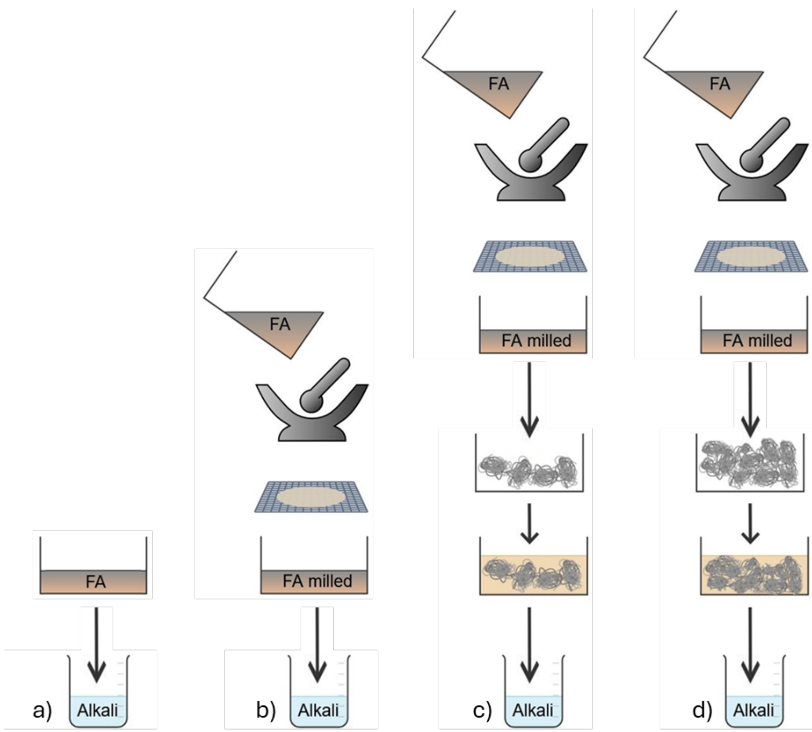

Figure 2: Synthesis scheme: a) as-received FA, without fibres, b) 1 m%, and c) 5 m% fibres.
Source: own.

Four mixtures were prepared with the same mass ratio of the precursor (FA and FA_{milled}) and alkali (1 to 0.35), as shown in Figure 2: a) using the FA as-received and without fibres, b) using the FA_{milled} and without fibres, c) using the FA_{milled} and 1 m% of fibres, and d) using FA_{milled} and 5 m% of fibres. The fibres and FA_{milled} were homogenised in a dry state before being activated with the liquid alkali. The precursor (with/without fibres) and the alkali were mixed for 2 minutes at up to 1000 rpm. The resulting slurry was moulded in silicone rubber moulds with 6 prisms ($2 \times 2 \times 8$ cm^3), and cured for 60 h at 70 °C in a conventional drying chamber, and then exposed to room conditions to cool before the mechanical tests were performed.

3 Results and discussion

With the exception of the AAM composite, which contained 5 m% CBR fibres, the samples showed no noticeable differences in appearance or parameters observable by the naked eye or by touch. As can be seen in Figure 3, the composite with the highest percentage of CBR fibres appeared "hairy," without sufficient binder throughout the volume, and felt soft when pressed between the fingers, suggesting that pavements made from a larger amount of CBR fibres in AAM material could provide a "cushioned" walking experience. The composite showed the ability to recover its shape under cyclic pressure between the fingers.

The mechanical strengths in the MPa and in % (normalised to the values of the AAM without fibres and from the as-received FA) are shown in Figures 4 and 5, respectively. While the compressive strength of the AAM from FA_{milled} increased compared to the AAM based on the as-received FA, the bending strength decreased, which could be due to the loss of non-combusted cellulose particles (large, non-spherical, but non-fibrous) during the mechanical milling of the FA. However, the difference between the mechanical strengths of the AAM from FA_{milled} and from FA is less significant than the difference between the AAM from FA or FA_{milled} and AAM with added fibres. Both the bending and compressive strength increased significantly in the AAM composites with 1 m% CBR fibres, while the "cushion" effect and the lack of binder in the AAM composites with 5 m% CBR fibres led to a significantly lower mechanical performance compared to the fibreless reference.

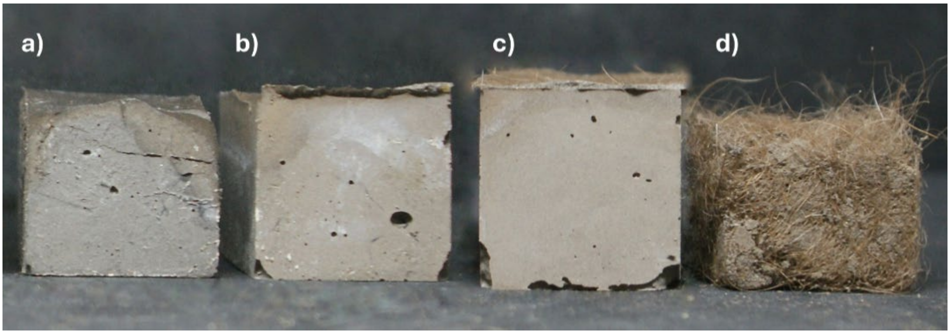

Figure 3: AAM composites with: a) as-received FA and without fibres, b) FA_{milled} and without fibres, c) FA_{milled} and 1 m% fibres, and d) FA_{milled} and 5 m% fibres.

Source: own.

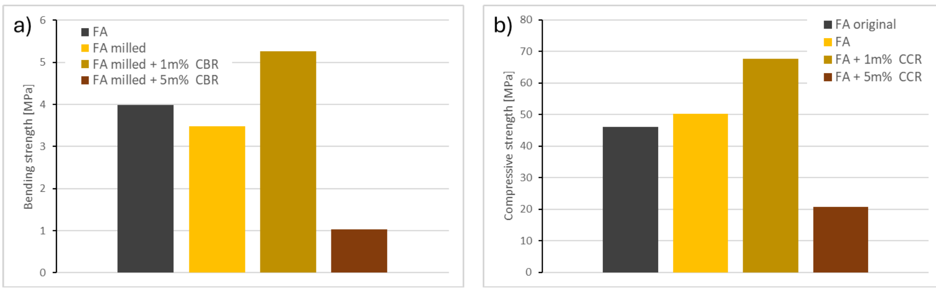

Figure 4: a) Bending, and b) compressive strength of AAM composites in MPa.

Source: own.

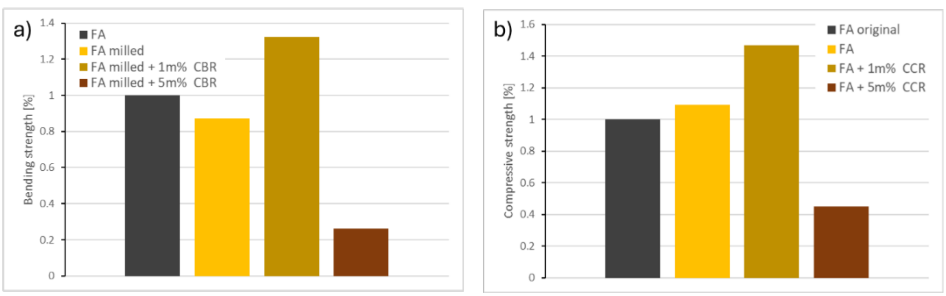

Figure 5: a) Bending, and b) compressive strength of the AAM composites in % (normalised to the values of the AAM without fibres).

Source: own.

When comparing the AAM composites with fibres with the AAM from the as-received FA, the bending strength of the AAM composite with 1 m% CBR fibres increased by more than 30% and the compressive strength by almost 50%. The addition of 5 m% CBR fibres reduced the bending strength by almost 30% and the compressive strength by almost 50%. The highest compressive strength achieved among all the AAM composites was, therefore, almost 70 MPa, and the bending strength was 5 MPa.

The geometric densities of the AAM composites are shown in Figure 6. While the difference in geometric density after the addition of 1 m% CBR fibres falls within the range of measurement error, the decrease in geometric density of almost 20% after the addition of 5 m% CBR fibres is far too large to be explained by measurement or sample preparation errors. In fact, the theoretical value of the densities of the composites is only lower to the 3rd decimal compared to the measured geometric density of the fibre-free AAM (the calculation was performed in kg/l). The current hypothesis is that the decrease in geometric density of the AAM composite with 5 m% CBR fibres is due to the lack of binder in the composite, which is replaced by air (as can also be seen in the photo in Figure 3d).

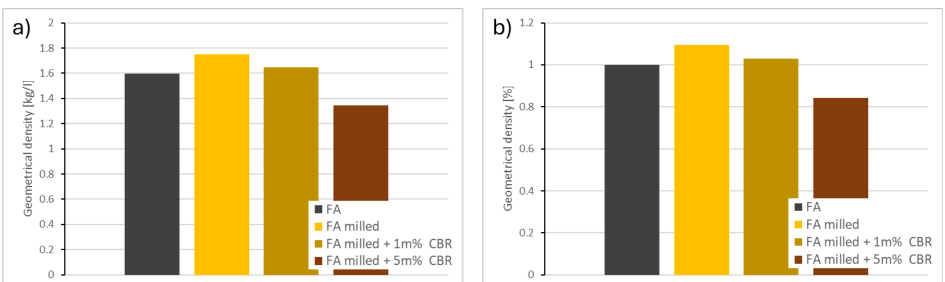

Figure 6: Geometric density of AAM composites in a) kg/l, and b) % (normalised to the values of the AAM without fibres).
Source: own.

Therefore, the decision on the required proportion of the CBR fibres in the AAM must be based on the desired functionality of the building product. A higher mass ratio of CBR fibres can be used for garden paths or insulation panels, but for products that require a higher mechanical performance, the addition of CBR fibres must be less than 5 m%.

4 Conclusion

This study demonstrated that even a small addition of fibres, specifically of dog hair with a functional, naturally water-resistant coat, can lead to unexpectedly high compressive strength values. However, the optimal fibre content and the influence of fibre length still need to be determined experimentally. Equally important is the assessment of the longevity (degradation) of such fibres in an alkaline environment.

Acknowledgment

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Data availability status

The original data presented in the study are openly available in the repository Zenodo at https://zenodo.org/records/17184936 with DOI: 10.5281/zenodo.17184936.

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Barbara Horvat, PhD, is a physicist and project leader at the High Voltage and Power Plants Department, in the nuclear group. Her research focuses on radioactive waste (management), (green) building materials, (electrical and thermal) insulation materials, especially fire-resistant electrical cables, semiconductors, the circular economy in material science, and life cycle assessment (LCA). She earned her BSc in Physics with a thesis on eye-safe LIDAR for aerosol detection, and her PhD in Nanophysics, studying photocatalytic degradation of organics using TiO_2 nanoparticles. Her postdoc involved chemical and mineralogical evaluation of primary and secondary raw materials for alkali-activated materials, including software development for recipe optimisation using XRF/XRD. She led teams to multiple circular economy awards for inventions, especially connected with the influence of the electromagnetic field on new materials.

Nadja Železnik, PhD, is a physicist, psychologist and project leader at the High Voltage and Power Plants Department, in the nuclear group. Her work focuses on radioactive waste (management), nuclear legislation, stakeholder engagement, risk perception, emergency preparedness, and communication in environmental and nuclear projects. She earned her BSc in Physics and MSc in Reactor Physics at the Faculty of Mathematics and Physics, and her PhD in Psychology at the Faculty of Arts. With over 35 years of experience, she has contributed to numerous national and international projects, developing legislation, feasibility studies, remediation plans, safety assessments and education and training programmes. She has coordinated multiple EU projects, and serves as an expert for the International Atomic Energy Agency.

Lara Petrič, BSc student, is studying at the Biotechnical Faculty, University of Ljubljana. As part of a summer research internship, she contributed to the synthesis and characterisation of alkali-activated materials within the ARIS project, including sample preparation, mechanical testing and chemical and crystallographic analyses. As a promising student, she has also begun contributing to abstracts and presentations for scientific conferences.

Sara Tominc, PhD, is a researcher at the Department of Materials, in the Laboratory for Cements, Mortars and Ceramics, at the Slovenian National Building and Civil Engineering Institute. Her research focuses on traditional ceramics, and on the beneficial use of waste materials in the construction industry. She obtained her BSc in Chemistry and Chemical Engineering at the University of Maribor and her PhD at the Jožef Stefan Institute, where she investigated the influence of pentavalent dopants on twinning and microstructure development in SnO_2 ceramics for high-performance varistors and dielectrics. She specialises in electron microscopy, thermal analysis and waste characterisation. Recently, she has been investigating accelerated mineral carbonation, aiming to understand the mechanisms and kinetics of CO_2 sequestration and to optimise carbonation conditions.

Summary

The study investigates alkali-activated fly ash (FA) composites reinforced with keratin-based fibres from Chesapeake Bay Retrievers. To increase reactivity, the FA was milled and sieved below 125 µm, while the fibres were incorporated at two mass ratios (1 m% and 5 m%) relative to the FA as part of the preliminary study. Mechanical tests on 3-day-old composites showed that the addition of 1 m%

fibres improved performance significantly, increasing the compressive strength by almost 50% (to ~70 MPa) and bending strength by over 30%. In contrast, the addition of 5 m% fibres resulted in a "hairy", low-binder structure with reduced geometric density and compressive strength. Nevertheless, the fibre-rich composite displayed a unique cushioning effect that restored shape under cyclic pressure, suggesting potential for non-structural applications such as pathways or insulation. The results demonstrated that small additions of keratin fibres can improve the performance of AAM, but excessive fibre content compromises its strength.